Reinvestigation of the Reactions of 1-Phenyl-3,4-dimethylphosphole with Dimethyl Acetylenedicarboxylate

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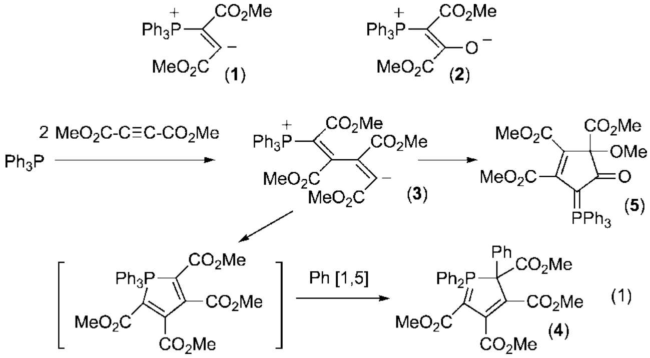
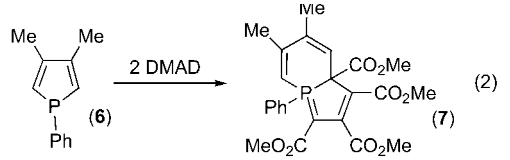
Received June 24, 2008

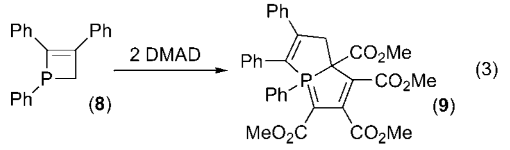
Summary: In contrast with an earlier report, the reaction of 1-phenyl-3,4-dimethylphosphole with an excess of dimethyl acetylenedicarboxylate (DMAD) at room temperature affords the phosphole + 2 DMAD ylide **10**, *whose structure was established by a careful analysis of the* ^{13}*C NMR spectrum. Its stability is surprising, since the analogous* Ph_3P *+ 2 DMAD adduct spontaneously rearranges to other products and has never been fully characterized. When the reaction of phosphole with DMAD was carried out in the presence of* $AgNO_3$*, the intermediate 1:1 adduct was oxidized to the stable oxo-ylide* **13**, *whose X-ray crystal structure shows the highly zwitterionic character.*

The 1:1 adduct between triphenylphosphine and dimethyl acetylenedicarboxylate (**1**) has a great deal of synthetic uses in organic chemistry[1] but has never been characterized as such, due to its instability. When the reaction is performed in the presence of copper(I) chloride, this transient adduct is oxidized to the stable oxo-ylide **2**, which has been adequately characterized by ^{13}C NMR.[2] When the reaction is performed with an excess of DMAD, a 1:2 adduct (**3**) is formed that rearranges to a 2*H*-phosphole (**4**) and to a cyclopentenylidenephosphorane (**5**) according to the classical work of Tebby[3] (eq 1).



The rearrangement to **4** probably proceeds via a pentacoordinate intermediate in which one of the phenyl substituents migrates from phosphorus to one of the α-carbons of the phosphole ring. A similar rearrangement has been found with 1-phenyl-3,4-dimethylphosphole (**6**), yielding the ring-expanded product **7**[4] (eq 2) and, more recently, with the dihydrophosphete **8**, giving also a ring-expanded product (**9**)[5] (eq 3). In this last case, a full characterization was provided by ^{13}C NMR and X-ray crystal structure analysis. The relief of the ring strain in the four-membered ring is certainly a driving force for the ring expansion, and a similar chemistry has also been reported with phosphetanes.[6]





We have a longstanding interest in the reactions of phosphole derivatives with DMAD because they serve for the synthesis of 7-phosphanorbornadiene complexes,[7] which, in turn, serve as precursors for terminal phosphinidene complexes, whose extensive carbene-like chemistry has been reviewed several times.[8] This led us to reinvestigate the reaction of phosphole **6** with DMAD. Our results are different from those reported in the literature.[4]

Results and Discussion

Since we needed ^{13}C NMR spectral references, we repeated the reaction of triphenylphosphine with DMAD (in CH_2Cl_2 at room temperature, overnight). After purification by chromatography (silica gel, 4:1 EtOAc−petroleum ether), we obtained a

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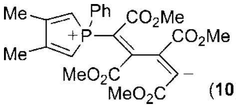
10.1021/om8005867 CCC: $40.75

yellow product whose ^{31}P and ^{1}H NMR data were closely similar to those reported by Tebby[3] for **5**. The ^{13}C NMR spectrum was entirely consistent with this formulation: $\delta(^{13}C)$ ($CDCl_3$) 51.15 (s, OMe), 51.84 (s, OMe), 52.52 (s, OMe), 70.69 (d, $^{1}J_{CP} = 118.5$ Hz, C═P), 77.28 (s, OMe), 87.15 (d, $^{3}J_{CP} =$ 12 Hz, sp^3 C(OMe)), 107.54 (d, $J_{CP} = 11.2$ Hz, C═C), 122.05 (d, $^{1}J_{CP} = 91.5$ Hz, Ph C ipso), 129.06 (d, $J_{CP} = 12.8$ Hz, CH(Ph)), 133.38 (d, $J_{CP} = 2.3$ Hz, *p*-CH(Ph)), 134.22 (d, J_{CP} = 10.5 Hz, CH(Ph)), 160.22 (d, $J_{CP} = 14.3$ Hz, C═C), 162.46 (d, $J_{CP} = 2.3$ Hz, CO), 166.29 (s, CO), 168.17 (s, CO), 195.08 (d, $^{2}J_{CP} = 7.5$ Hz, CO). Particularly significant are the carbonyl at δ 195.08, the quaternary carbon at δ 87.15, and the ylidic carbon at δ 70.69, with its huge coupling with phosphorus.

We then investigated the reaction of an excess of DMAD with phosphole **6** under the same conditions. The proton spectrum of the product **10** showed a phosphole to DMAD ratio of 1:2. The two methyl groups gave only one peak at δ 2.22 and the two olefinic CH groups one doublet at δ 6.67 ($^{2}J_{HP} =$ 27.9 Hz). The ring-expanded dissymmetrical formula **7** was thus ruled out. The ^{13}C NMR spectrum confirmed that the phosphole ring is intact in **10**. The assignments were controlled using ^{1}H−^{13}C correlated spectra. The huge coupling of the phenyl ipso carbon with phosphorus clearly indicates that the phenyl group is connected to phosphorus. The spectrum also displays four sets of resonances corresponding to the four methoxycarbonyl groups. A HMBC experiment showed that the four carbonyls are correlated with the four methoxy groups. The carbonyl at δ 169.87 is correlated with the methoxy at δ 63.65. The four COOMe groups are intact. The absence of a resonance around δ 195 means that **10** does not contain a keto group as does **5**. Finally, the spectrum shows four unsaturated carbons bearing no hydrogen at $\delta(^{13}C)$ 76.88 (d, $^{1}J_{CP} = 114$ Hz, C═P), 107.11 (d, $J_{CP} = 14.3$ Hz, C═C), 109.10 (d, $J_{CP} = 8.3$ Hz, C═C), and 126.59 (d, $J_{CP} = 12$ Hz, C═C). The only possible formula compatible with these data is that of a 1:2 adduct analogous to **3**. The question, then, is why **10** is stable at room temperature whereas **3** must be kept at −50 °C. Phospholium salts are destabilized by their somewhat antiaromatic character.[9] Thus, one possible explanation is that the charge separation in **10** is reduced by comparison with that in **3**. The Coulombic attraction which favors the formation of the pentacoordinate intermediate from **3** would be reduced in **10**: hence, a better stability.



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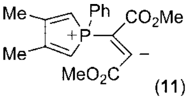

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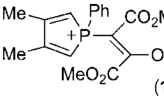

(13)

We then decided to duplicate the reaction of triphenylphosphine with DMAD in the coordination sphere of copper(I).[2] The oxidation of the transient 1:1 adduct **11** does not take place, and the 1:2 adduct **10** is the final product of the reaction. This higher resistance of **11** toward oxidation by comparison with **1** might be ascribed to the negative charge at the β-carbon of the ylide being lower in **11** than in **1**. We then decided to replace CuCl by the stronger oxidant $AgNO_3$. The 1:1 complexes of phosphole **6** with silver(I) are known.[10] The 1:1 complex of **6** and $AgNO_3$ (**12**) was prepared and reacted in situ with DMAD. Its characterization was limited to its NMR spectra. As expected, the reaction of **12** with DMAD produced the oxo-ylide **13**. The ^{1}H NMR spectrum in $CDCl_3$ showed the phosphole methyls as a singlet at δ 2.10, the two methoxy groups as singlets at δ 3.57 and 3.79, and the two phosphole olefinic protons as a doublet at δ 6.63 ($^{2}J_{HP} = 27.6$ Hz). The ^{13}C NMR spectrum showed the carbonyl at δ 183.38 ($^{2}J_{CP} = 6$ Hz) and the ylidic carbon at δ 66.12 ($^{1}J_{CP} = 107.6$ Hz). We were able to get good crystals of **13** for X-ray analysis (Figure 1). The ylidic carbon is strictly planar (sum of angles 359.44°). The $C_{15}O_5$ bond is long at 1.234(3) Å, vs 1.198(2) Å for $C_{16}O_4$. The ylidic bond is very long at 1.7514(17) Å, vs 1.661 Å for $Ph_3P{=}CMe_2$.[11] Thus, it is clear that **13** has a highly zwitterionic structure, as shown. At 3.008 Å, there is probably some Coulombic interaction between the negative oxygen and the positive phosphorus, thus explaining the *Z* stereochemistry of the $C_{13}{=}C_{15}$ double bond. As far as we know, this is the first time that this type of oxo-ylide has been structurally characterized.

Two conclusions can be drawn from this series of experiments. First, the reaction of phosphole **6** with DMAD in excess initially gives the nonrearranged 1:2 adduct **10**. The previously described ring-expanded product **7** is only a subsequent product of this reaction. The thermal stability of **10** comes in sharp contrast with the instability of the 1:2 adduct of triphenylphosphine (**3**). In the same vein, the transient 1:1 adduct is more resistant toward oxidation with phosphole than with triphenylphosphine. The second conclusion is that the replacement of Ph_3P by phosphole **6** might significantly alter the chemistry of **1** and its synthetic applications.

Experimental Section

All reactions were routinely performed under an inert atmosphere of nitrogen by using standard Schlenk techniques and dry deoxygenated solvents. Xylene and CH_2Cl_2 were dried over P_2O_5. Nuclear magnetic resonance spectra were recorded on a Bruker 300 MHz spectrometer. Chemical shifts are expressed with respect to external TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P). All coupling constants (*J* values) are reported in hertz (Hz). Elemental analyses were performed on an Elementar Analysensteme GmbH VarioEL III instsrument. Mass spectra were recorded on a LC-MSD-Trap-XCT instrument by electrospray ionization (ESI). Phosphole **6** was prepared according to the literature.[12]

Ylide 10. At room temperature, DMAD (2.6 mL, 21.1 mmol) was added to a CH_2Cl_2 (15 mL) solution of phosphole (0.8 mL, 4.24 mmol). The solution turned dark immediately. After 10 min, two peaks (δ 19 and 37 ppm) appeared in the ^{31}P NMR spectrum. The reaction mixture was stirred overnight, and the peak at 37 ppm disappeared. After purification on TLC (4:1 EtOAc−petroleum ether), **10** was obtained as a yellow solid (452 mg, 22%).

$\delta(^{31}P)$ ($CDCl_3$): 18.2. $\delta(^{1}H)$ ($CDCl_3$): 2.22 (s, 6H, Me), 3.61 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.90 (s, 3H, OMe), 6.67 (d, $^{2}J_{HP} = 27.9$ Hz, 2H, ═CHP), 7.29−7.49 (m, 5H, Ph). $\delta(^{13}C)$ ($CDCl_3$): 17.88 (d, $^{3}J_{CP} = 18$ Hz, Me), 50.85 (s, OMe), 51.33 (s, OMe), 52.22 (s, OMe), 63.65 (s, OMe), 76.88 (d, $^{1}J_{CP} =$ 114 Hz, C═P),107.11 (d, $J_{CP} = 14.3$ Hz, C═C), 109.10 (d, $J_{CP} =$ 8.3 Hz, C═C), 118.51 (d, $^{1}J_{CP} = 89.3$ Hz, ═CHP), 122.27 (d, $^{1}J_{CP}$ = 93.8 Hz, Ph C ipso), 126.59 (d, $J_{CP} = 12$ Hz, C═C), 129.20 (d, $J_{CP} = 13.5$ Hz, Ph CH), 130.86 (d, $J_{CP} = 12$ Hz, Ph CH), 132.77 (d, $^{4}J_{CP} = 3$ Hz, Ph CH para), 157.82 (d, $^{2}J_{CP} = 18.8$ Hz, ═C(Me)), 159.05 (d, $J_{CP} = 7.5$ Hz, CO), 163.85 (d, $J_{CP} = 3$ Hz, CO), 165.38 (s, CO), 169.87 (d, $J_{CP} = 3$ Hz, CO).

Oxo-Ylide 13. To a CH_2Cl_2 (10 mL) solution of phosphole (0.5 mL, 2.65 mmol) was added $AgNO_3$ (448 mg, 2.65 mmol). The

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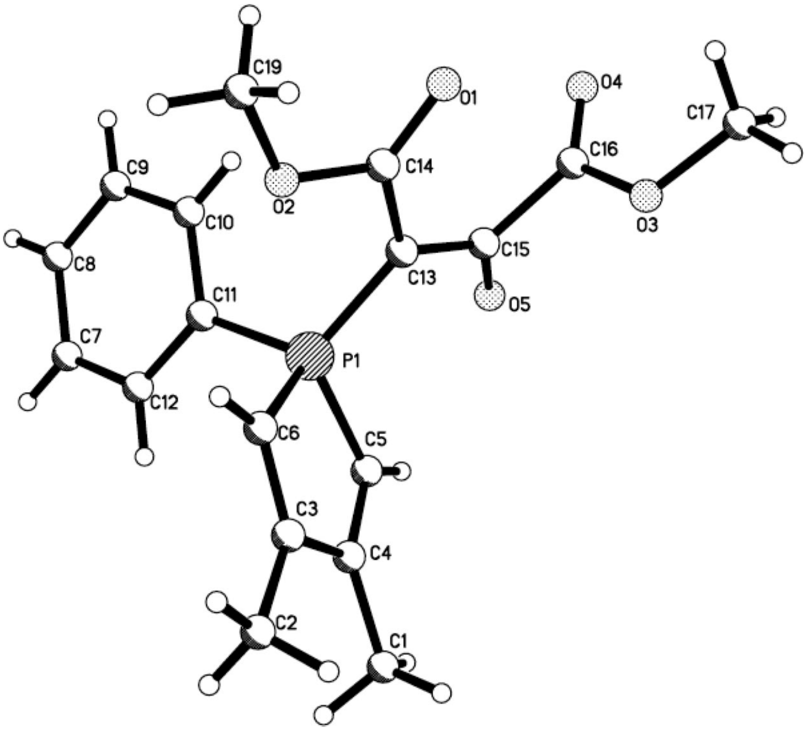

Figure 1. X-ray crystal structure of oxo-ylide **13**. Main bond lengths (Å) and angles (deg): P1−C5 = 1.782(2), P1−C6 = 1.7860(19), P1−C13 = 1.7514(17), C13−C15 = 1.417(3), C15−C16 = 1.521(3), C15−O5 = 1.234(3), C16−O4 = 1.198(2); C5−P1−C6 = 93.22(9), C5−P1−C13 = 114.19(11), C6−P1−C13 = 115.86(8), P1−C13−C15 = 117.52(15), P1−C13−C14 = 120.07(16), C13−C15−O5 = 126.06(18), C13−C15−C16 = 118.67(18).

reaction mixture was stirred at room temperature in the dark for 1 h, and one new ^{31}P peak appeared at 7.5 ppm. The NMR data for **12** are as follows. δ(^{1}H) ($CDCl_3$): 2.14 (s, 6H), 6.40 (d, $^{2}J_{HP}$ = 38.4 Hz, 2H, =CHP), 7.29−7.42 (m, 5H, Ph). δ(^{13}C) ($CDCl_3$): 17.71 (d, $^{3}J_{CP}$ = 11.3 Hz, Me), 124.16 (d, $^{1}J_{CP}$ = 36.8 Hz, =CHP), 125.11 (d, $^{1}J_{CP}$ = 36.8 Hz, Ph C ipso), 129.05 (d, J_{CP} = 11.3 Hz, Ph CH), 131.24 (d, $^{4}J_{CP}$ = 2.3 Hz, Ph CH para), 133.58 (d, J_{CP} = 16.5 Hz, Ph CH), 153.55 (d, $^{2}J_{CP}$ = 9 Hz, =C(Me)). After evaporation of CH_2Cl_2 under vacuum, xylene (15 mL) and DMAD (0.36 mL, 2.928 mmol) were added. The reaction mixture was stirred at 80 °C in the dark for 3.5 h. A new ^{31}P peak appeared at 24.3 ppm. After filtration, the resulting yellow solution was concentrated under reduced pressure. The residue was purified by TLC using petroleum ether−ethyl acetate (1:1.8) as the eluent to afford the white product **13** (202 mg, 22%). δ(^{31}P) ($CDCl_3$): 24.3. δ(^{1}H) ($CDCl_3$): 2.10 (s, 6H, Me), 3.57 (s, 3H, OMe), 3.79 (s, 3H, OMe), 6.63 (d, $^{2}J_{HP}$ = 27.6 Hz, 2H, =CHP), 7.20−7.63 (m, 5H, Ph). δ(^{13}C) ($CDCl_3$): 16.93 (d, $^{3}J_{CP}$ = 18.2 Hz, Me), 49.96 (s, OMe), 50.95 (s, OMe), 66.12 (d, $^{1}J_{CP}$ = 107.6 Hz, P=C), 117.18 (d, $^{1}J_{CP}$ = 89.8 Hz, =CHP), 120.11 (d, $^{1}J_{CP}$ = 86.2 Hz, Ph C ipso), 128.37 (d, J_{CP} = 13 Hz, Ph CH), 130.28 (d, J_{CP} = 11.8 Hz, Ph CH), 132.01 (d, $^{4}J_{CP}$ = 3.1 Hz, Ph CH para), 156.87 (d, $^{2}J_{CP}$ = 18.4 Hz, =C(Me)), 166.69 (2d, J_{CP} = 16.5 and 13.5 Hz, 2 CO(OMe)), 183.38 (d, $^{2}J_{CP}$ = 6 Hz, C=O). MS *m/z:* 369.3 ([M + Na]$^{+}$).

Acknowledgment. This paper is dedicated to Professor Yangjie Wu on the occasion of his 80th birthday. We thank the National Natural Science Foundation of China (Grant No. 20702050) and Zhengzhou University for financial support.

Supporting Information Available: CIF file giving data for the X-ray crystal structure analysis of compound **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8005867